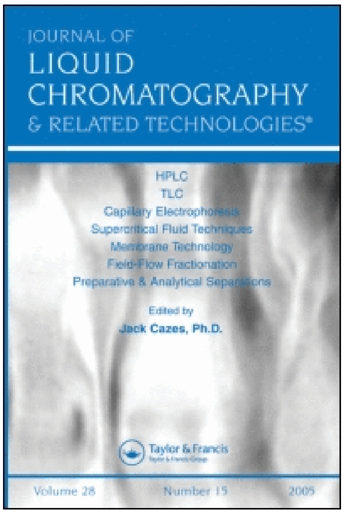

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REMOVAL OF AGGREGATES FROM MICRON-SIZED POLYMETHYL METHACRYLATE (PMMA) LATEX BEADS USING FULL FEED DEPLETION MODE OF GRAVITATIONAL SPLITT FRACTIONATION (FFD-GSF)

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□ *Split-flow thin cell (SPLITT) fractionation (SF) provides separation of colloidal particles or macromolecules into two fractions. A gravitational SF (GSF) system was constructed and its applicability was tested for removal of aggregates from mass-produced polymethyl methacrylate (PMMA) latex beads. The full-feed depletion (FFD) mode of GSF (FFD-GSF) was found to be a simpler alternative to the conventional mode for removal of the aggregates. Unlike in the conventional mode, where two inlets are used for feeding of the sample suspension and the carrier liquid respectively, only one inlet (for the sample feeding) is used in the FFD mode, allowing easier control of the flow rate. Also the sample suspension is not diluted during FFD mode operation. Aggregated particles were found only in one of the two fractions, allowing removal of the aggregates. The sample was continuously fed into the GSF system, showing potential application to a large quantity operation for removal of the PMMA aggregates.*

Keywords aggregate, binary separation, full-feed depletion (FFD), large quantity-removal, polymethyl methacrylate (PMMA) latex beads, SPLITT fractionation (SF)

INTRODUCTION

Polymeric latex beads play important roles in various industries including the paints and coatings, ceramic processing, and biotechnology.[1] Polymeric microbeads with uniform sizes have found widespread applications such as in modeling physical phenomena, calibrating measuring instruments, and in immunoassays on medical diagnostic test.[1–2]

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Sometimes mass-production of polymeric microbeads is hampered by the presence of beads having non-uniform sizes and even some aggregates. Often, for best performance of the latex beads, those aggregates must be removed.

Split-flow thin cell (SPLITT) fractionation (SF) is a family of techniques that can be employed for large quantity-separation of colloidal particles and macromolecules into two subpopulations based on their sizes.[3–8] SF has been used for separation of proteins,[7,9–11] glass beads,[6,8] starch granules,[6,12] liposomes,[13] cells,[14–16] silica particles,[17] magnetic particles,[18] and environmental particles.[19–21]

SF is carried out in a thin ribbon-like channel (0.1 ~ 1 mm thick) across which an external field is applied.[3–8] There are a few subtechniques of SF based on the type of the external field employed, including gravitational SF (GSF), centrifugal SF (CSF), and electrical SF (ESF). In GSF, the Earth's gravity is used as the external field.

The expanded side views of the GSF channel are shown schematically in Figure 1. GSF can be operated in two different modes: conventional mode

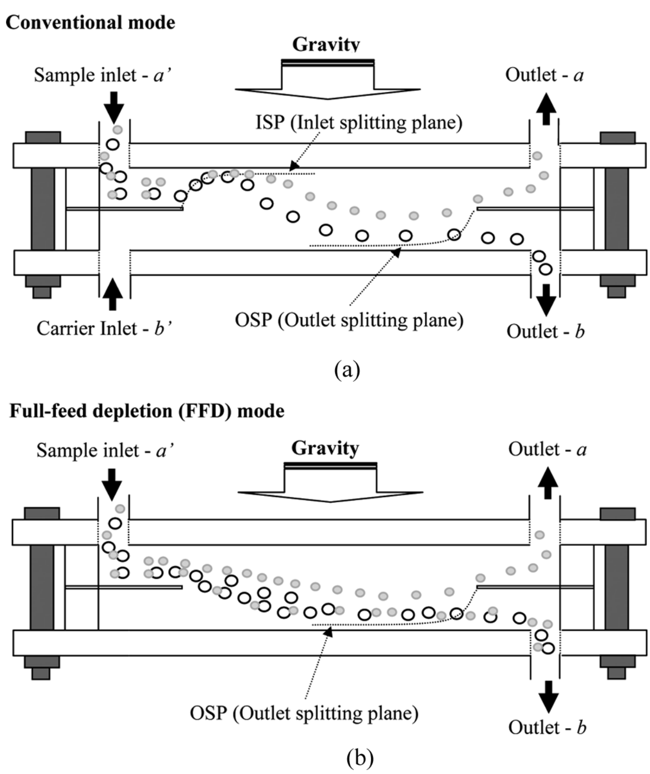

FIGURE 1 Expanded side views of GSF channels operating in the conventional mode (a) and the full-feed depletion (FFD) mode (b).

and the full-feed depletion (FFD) mode.[22,23] The FFD mode provides merits over the conventional mode. The FFD mode is simpler to operate since only one inlet flow is used for the sample feeding, requiring only one pump and allows easier control of the flow rates. Also, there is no sample dilution as there is no incoming flow of the carrier liquid. In the conventional mode, sample dilution is unavoidable due to the presence of the incoming flow of the carrier liquid

In this work, a GSF system was constructed and its operation in the FFD mode was tested for removal of aggregates from mass-produced polymethyl methacrylate (PMMA) latex beads.

THEORY

Figure 1(a) shows the GSF operating in the conventional mode, where the sample suspension is fed through the inlet-a' at the flow rate of $V(a')$ while the carrier liquid is fed through the inlet-b' at the flow rate of $V(b')$. The "inlet splitting plane (ISP)" in Figure 1(a) denotes an imaginary line dividing the two inlet streams. Usually in the conventional mode operation, $V(b')$ is much higher than $V(a')$ to compress the sample toward the top wall of the channel above the ISP. While migrating down the channel by the flow, particles are forced to settle by the external field. When the fluid stream reaches the outlet splitter, it is divided into two fractions by the outlet splitter. The "outlet splitting plane (OSP)" denotes the line separating the two outlet flows. Sample particles settling fast enough to cross the OSP will exit the outlet-b, and the rest will exit the outlet-a, thus providing separation of the particles into two fractions (fraction-a and b) based on their settling velocities.

For spherical particles having the same densities, their settling velocities depend only on the size. In the conventional mode of GSF, the cut-off diameter, d_c is given by[5]

$$d_c = \sqrt{\frac{18\eta}{bLG\Delta\rho}(V(a) - 0.5V(a'))}, \tag{1}$$

where η is the viscosity of the carrier liquid, b the channel breadth, L the channel length, G the Earth's gravity, $\Delta\rho$ the density difference between the sample and the carrier liquid, $V(a')$ the volumetric flow rate (in mL/min) exiting the outlet-a. Thus SF provides size-based separation into two fractions, with the fraction-a containing particles having diameters smaller than d_c, and the fraction-b containing those larger than d_c. By using Eq. (1), the flow rates needed for separating particles at d_c can be calculated.

Figure 1(b) shows the GSF channel operating in the FFD mode.[23] Unlike in the conventional mode, only one inlet (inlet-a') is used in the FFD mode for the sample feeding. In the FFD mode, the cut-off diameter, d_c is given by[18]

$$d_c = \sqrt{\frac{18\eta}{bLG\Delta\rho}(V(a') - 0.5V(b))} \tag{2}$$

Again, the flow rates required for separating particles with the cut-off diameter d_c in the FFD mode can be calculated by using Eq. (2). One of the shortcomings of the FFD mode is that the resolution is expected to be lower in the FFD mode than in the conventional mode.[18] In the FFD mode, particles are not compressed towards the top wall of channel, resulting in some of particles smaller than d_c being eluted in the fraction-*b*. The fraction-*a* will still contain only those smaller than d_c. The FFD mode has been employed rather successfully for some applications,[18,24–25] Recycling of the fraction-*b* (by feeding the fraction-*b* through the inlet-a' for a repeated SF operation at the same flow rate conditions) has been suggested to improve the resolution.[18]

EXPERIMENTAL

Chemicals and Materials

PMMA latex beads having the average density of 1.18 g/mL were mass-produced for industrial applications. Figure 2 shows optical micrographs of the PMMA latex beads obtained at the magnification of 400 times. As shown in Figure 2, the PMMA latex beads are spherical, and contain some snowman-like aggregated particles (circled). Figure 3 shows the size distribution obtained from optical microscopy (OM) for the particles shown in Figure 2 by measuring about 1,000 particles. For aggregates, the longest dimension was taken as the diameter. The OM analysis of the PMMA beads gave the mean diameter of 3.8 μm, standard deviation of 0.36 μm, and the coefficient of variation (CV) of 9.35%. About 1% of the particles were found to be aggregates. For GSF separation, the PMMA latex beads were dispersed at the concentration of 0.5% (w/v) in an 8:2 mixture of the GSF carrier liquid and ethanol.

Apparatus

The GSF channel used in this study was constructed in the laboratory as shown in Figure 4. The channel was assembled by clamping two glass plates,

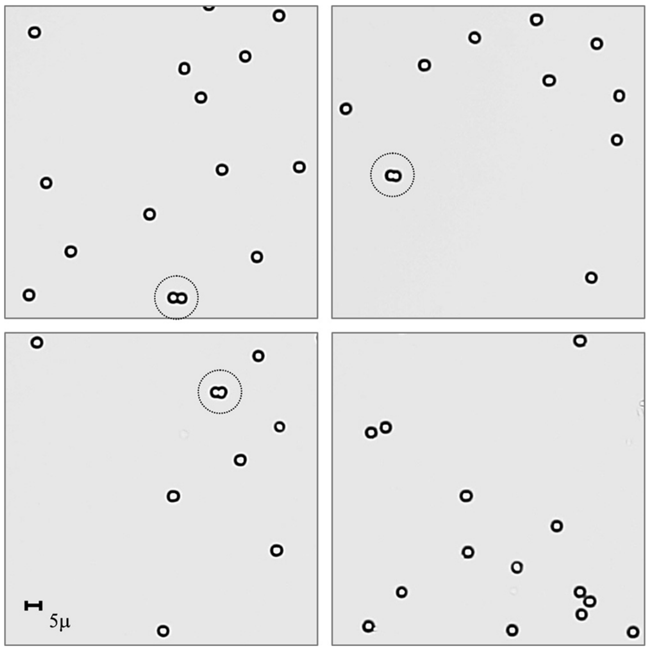

FIGURE 2 Optical micrographs (×400) of mass-produced PMMA latex beads.

two Mylar spacers and one stainless steel sheet (used as the flow-splitter) between two Plexiglas™ blocks. The thicknesses of the stainless steel splitter and the Mylar spacers were same at 127 μm, resulting in the total

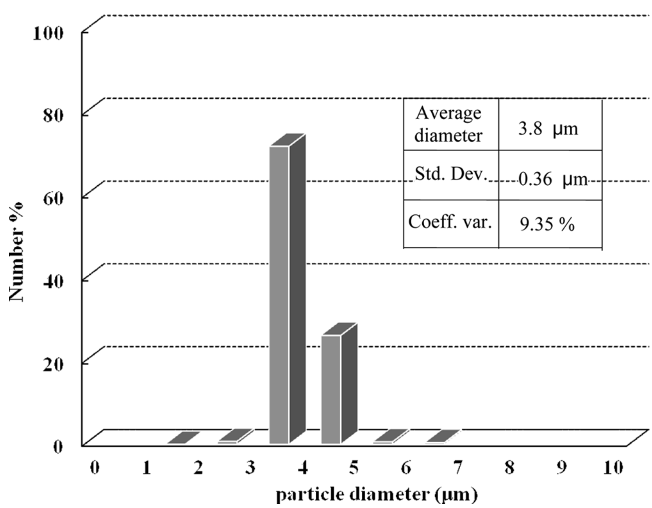

FIGURE 3 Size distribution of PMMA latex beads shown in Figure 2 determined by optical microscopy. 1,000 particles were measured.

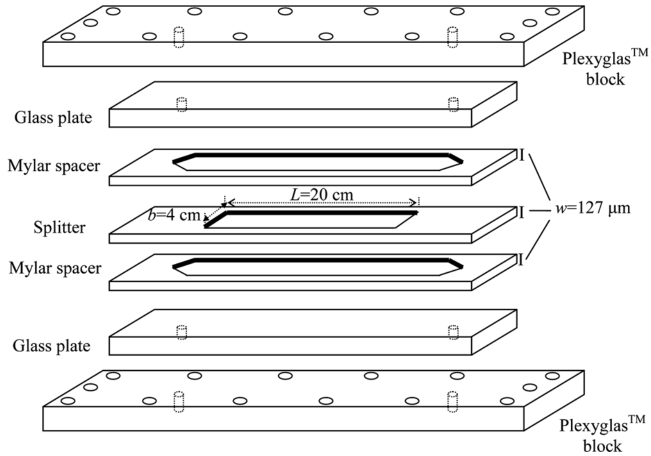

FIGURE 4 Diagram of GSF channel assembly used in this study. The channel has dimensions of width $(w) = 0.0381$ cm, breadth $(b) = 4$ cm, and length $(L) = 20$ cm, respectively.

thickness of the channel to be 381 μm. The channel was 20 cm long and 4 cm wide. The flow through the inlet-a′ was provided by a Minipuls 3 peristaltic pump (Gilson Medical Electronics, Middleton, WI, USA).

The carrier liquid was an aqueous solution of 0.1% (w/v) FL-70 (Fisher Scientific, Fair Lawn, NJ, USA) and 0.02% (w/v) sodium azide (NaN_3). FL-70 was used as a dispersing agent and NaN_3 as a bactericide. The viscosity and the density of the carrier liquid were taken to be 0.01 poise and 1.00 g/mL, respectively in all calculations. The GSF system was maintained at room temperature at all times.

The optical microscopy (OM) was performed by using an Olympus BX51TF optical microscopy (Shinjuku Monolith, Shinjuku-ku, Japan). For OM analysis of the size distribution of the PMMA latex beads, the sizes of nearly 1,000 particles were measured with the Image Inside™ software (Focus, Daejeon, Korea).

RESULTS AND DISCUSSION

In the FFD mode operations, usually the cut-off diameter d_c and the sample-feeding flow rate $V(d')$ are chosen first, then $V(b)$ is determined using Eq. (2). Once $V(b)$ is determined, $V(a)$ becomes $V(d')-V(b)$. As shown in Figures 2 and 3, most of the single (unaggregated) PMMA particles are smaller than about 4 μm in diameter, thus d_c was chosen to be 4 μm, so that all aggregated particles would exit through the outlet-*b*.

It is noted that a care must be taken in choosing the sample-feeding flow rate, $V(d')$. Higher $V(d')$ is desired as it allows higher sample throughput (TP, mass of the sample that can be processed by GSF in a unit time). At the same time, V(a′) must be kept below the level above which the flow becomes turbulent. It has been suggested that the Reynolds number (R_e) be lower than about 1,500 for a flow to be laminar.[26–27] R_e can be calculated by $Re = (\rho D_h \langle v \rangle)/\eta$,[28] where ρ is the density of the carrier, $\langle \nu \rangle$ the mean flow velocity, and D_h the hydraulic diameter.[29] In normal operating conditions of GSF, R_e is usually much lower than the limit due to the thin dimension of the GSF channel. More often V(a′) is limited by more practical reasons such as the back pressure. It is also noted that V(a′) can not be too low as the sample beads tend to settle down and precipitate on the bottom of the channel at too low flowrates. In this study, V(a′) was chosen to be 3 mL/min at which R_e is calculated to be 2.47. With d_c of 4 µm and V(a′) of 3 mL/min, Eq. (2) gives V(b) of 2.25 mL/min, and thus V(a) of 0.75 mL/min.

Figure 5 shows the optical micrographs of the original PMMA sample and its two GSF fractions-*a* and *b*. The size distributions of those GSF fractions determined by OM are shown in Figure 6. It can be seen in Figure 5 that the fraction-*a* contains only the single particles. Out of about 1,000

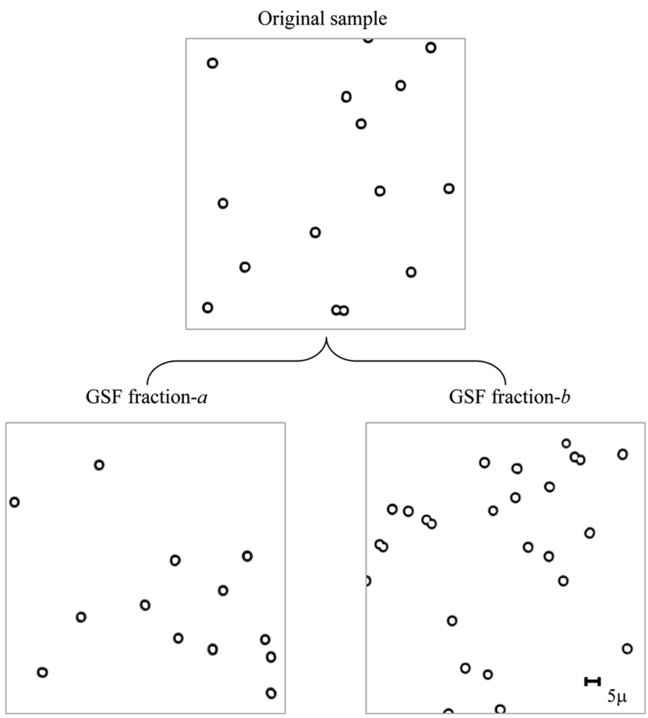

FIGURE 5 Optical micrographs (×400) of the original PMMA latex sample and its two GSF fractions-*a* and *b*. GSF conditions: $V(a') = 3.00$, $V(a) = 0.75$, $V(b) = 2.25$ mL/min, Carrier = water containing 0.1% (w/v) FL-70 + 0.02% (w/v).

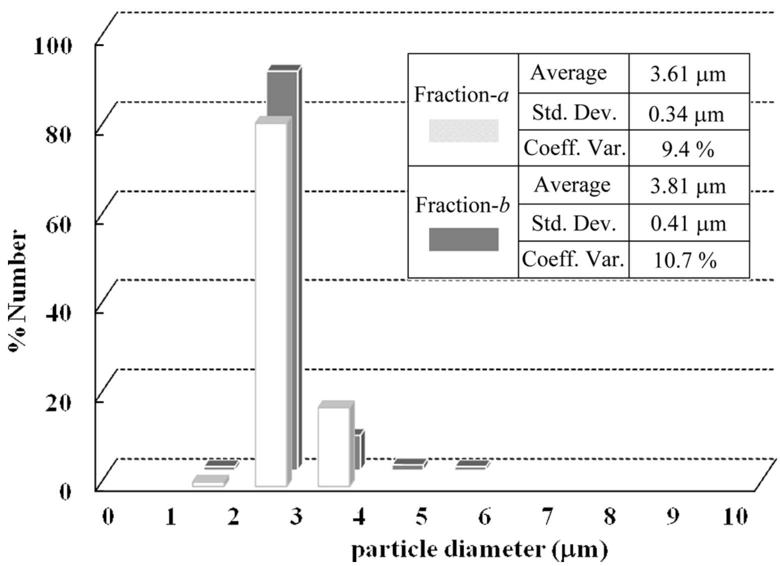

FIGURE 6 Size distributions of GSF fractions-*a* and *b* shown in Figure 5 determined by optical microscopy.

particles measured, no particles larger than 4 μm were found in the fraction-a as shown in Figure 6, and thus the fraction-a is considered to be purely of the single particles without aggregates. Particles larger than 4 μm (mainly the aggregates) were found only in the fraction-b as shown in Figures 5 and 6.

It is noted that the fraction-*b* contains significant amount of the single particles as well as the aggregates, as shown in Figures 5 and 6, which is typical of the FFD mode as mentioned earlier. One may recycle the fraction-*b* (by re-feeding the fraction-*b* through the inlet- *a*′) to recover more of the single particles.[18]

CONCLUSION

Results show GSF is applicable for removal of aggregates from PMMA latex beads. For this purpose, the FFD mode of GSF (FFD-GSF) seems to provide a good alternative to the conventional mode. Because FFD-GSF requires only one pump (instead of two required in the conventional mode), the flow rate control is simpler and, more importantly in some cases, the sample suspension is not diluted (if not concentrated). The only drawback of the FFD mode seems to be that a complete recovery of the single particles may not be possible due to co-elution of the single particles with the aggregated ones through the exit-*b*. One may be able to increase the recovery rate by recycling the fraction-b. Even then a complete recovery may not be possible.

FFD-GSF could be applied not only for the removal of large contaminants but also for narrowing the distribution of various types of micron-sized colloidal particles. More work is planned for implementation of a GSF system that is intended to use only in the FFD mode. By removing the inlet splitter, the design of the GSF channel will become simpler. An enlargement of the GSF channel will also be easier, which will allow higher sample throughput (TP)

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REFERENCES

1. Ugelstad, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T.N.; Mork, P.C.; Stenstad, P.; Hornes, E.; Olsvik, O. Preparation and application of new monosized polymer particles. Prog. Polym. Sci. **1992**, *17*, 87.
2. Liu, X.Q.; Guan, Y.P.; Yang, Y.; Ma, Z.Y.; Wu, X.B.; Liu, H.Z. Preparation of super paramagnetic immunomicrospheres and application for antibody purification. J. Appl. Polym. Sci. **2004**, *94*, 2205.
3. Giddings, J.C. A system based on split-flow lateral-transport thin (SPLITT) separation cells for rapid and continuous particle fraction. Sep. Sci. Technol. **1985**, *20*, 749.
4. Giddings, J.C. Optimization of transport-driven continuous SPLITT fraction. Sep. Sci. Technol. **1992**, *27*, 1489.
5. Springston, S.R.; Myers, M.N.; Giddings, J.C. Continuous particle fractionation based on gravitational sedimentation in split-flow thin cells. Anal. Chem. **1987**, *59*, 344.
6. Fuh, C.B.; Myers, M.N.; Giddings, J.C. Analytical SPLITT fractionation: Rapid particle size analysis and measurement of oversized particles. Anal. Chem. **1992**, *64*, 3125.
7. Fuh, C.B.; Levin, S.; Giddings, J.C. Rapid diffusion coefficient measurements using analytical SPLITT fractionation: Application to proteins. Analytical Biochemistry **1993**, *208*, 80.
8. Gao, Y.; Myers, M.N.; Barman, B.N.; Giddings, J.C. Continuous fractionation of glass microspheres by gravitational sedimentation in split-flow thin (SPLITT) cells. Particulate Science and Technology **1991**, *9*, 105.
9. Levin, S.; Myers, M.N.; Giddings, J.C. Continuous separation of proteins in electrical split-flow thin (SPLITT) cell with equilibrium operation. Sep. Sci. Technol. **1989**, *24*, 1245.
10. Williams, P.S.; Levin, S.; Lenczycki, T.; Giddings, J.C. Continuous SPLITT fractionation based on a diffusion mechanism. Ind. Eng. Chem. Res. **1992**, *31*, 2172.
11. Fuh, C.B.; Giddings, J.C. Isoelectric split-flow thin (SPLITT) fractionation of proteins. Sep. Sci. Technol. **1997**, *32*, 2945.
12. Contado, C.; Riello, F.; Dondi, F. Preliminary SPLITT cell separation of starch particles. Proceedings of the Seventh International Symposium on Field-Flow Fractionation, University Park Hotel, Salt Lake City, Utah, USA, **1998**.
13. Levin, S.; Tawil, G. Analytical SPLITT fractionation in the diffusion mode operating as a dialysis-like system devoid of membrane. Application to drug-carring liposomes. Anal. Chem. **1993**, *65*, 2254.

14. Levin, S.; Giddings, J.C. Continuous separation of particles from macromolecules in split-flow thin (SPLITT) cells. J. Chem. Tech. Biotechnol. **1991**, *50*, 43.
15. Zhang, J.; Williams, P.S.; Myers, M.N.; Giddings, J.C. Separation of cells and cell-sized particles by continuous SPLITT fractionation using hydrodynamic lift forces. Sep. Sci. Technol. **1994**, *29*, 2493.
16. Fuh, C.B.; Trujillo, E.M.; Giddings, J.C. Hydrodynamic characterization of SPLITT fractionation cells. Sep. Sci. Technol. **1995**, *30*, 3861.
17. Jiang, Y.; Kummerow, A.; Hansen, M.E. Preparative particle separation by continuous SPLITT fractionation. J. Micro Sep. **1997**, *9*, 261.
18. Jiang, Y.; Miller, M.E.; Hansen, M.E.; Myers, M.N.; Williams, P.S. Fractionation and size analysis of magnetic particles using FFF and SPLITT technologies. J. Magnetism and Magnetic Materials **1999**, *194*, 53.
19. Keil, R.G.; Tsamakis, Fuh, C.B.; Giddings, J.C.; Hedges, J.I. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. Geochimica et Cosmochimica Acta **1994**, *58*, 879.
20. Contado, C.; Dondi, F.; Beckett, R.; Giddings, J.C. Separation of particulate environmental samples by SPLITT fractionation using different operating modes. Analytical Chimica Acta **1997**, *345*, 99.
21. Dondi, F.; Contado, C.; Blo, G.; Garcia Martin, S. SPLITT cell separation of polydisperse suspended particles of environmental interest. Chromatographia **1998**, *48*, 643.
22. Fuh, C.B.; Myers, M.N.; Giddings, J.C. Centrifugal SPLITT fractionation: New technique for separation of colloidal particles. Ind. Eng. Chem. Res. **1994**, *33*, 355.
23. Myers, M.N.; Jiang, Y.; Giddings, J.C. Preparative particle separations by SPLITT fractionation. Proceedings of the Fifth International Symposium on Field-Flow Fractionation, Poster n. 31, Park City, Utah, USA, **1995**.
24. Blo, G.; Contado, C.; Grandi, D.; Fagioli, F.; Dondi, F. Dimentional and elemental characterization of suspended particulate matter in natural waters: Quantitative aspects in the integrated ultrafiltration, split-flow thin cell and inductively coupled plasma-atomic emission spectrometry approach. Analytical Chimica Acta **2002**, *470*, 253.
25. Lead, J.R.; Momi, A.D.; Goula, G.; Baker, A. Fractionation of freshwater colloids and particles by SPLITT: Analysis by electron microscopy and 3D excitation-emission matrix fluorescence. Analytical Chemistry **2006**, *78*, 3609.
26. Nguyen, N.T.; Werely, S.T. *Fundamentals and Applications of Microfluidics*; Artech House: Boston, 2002.
27. Giddings, J.C. *Unified Separation Science*; Wiley: New York, 1991.
28. Reynolds, O. An experimental investigation of the circumstances which determine whether the motion of water shall be direct or sinuous, and of the law of resistance in parallel channels. Proceedings of the Royal Society of London **1883**, *35*, 84.
29. White, F.M. *Viscous Fluid Flow*, 2nd Ed.; McGraw-Hill, 1991.